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Monitoring System for Collection and Analyses of Ambient Ethylene Dichloride (EDC) Levels in the Urban Atmosphere

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16. ABSTRACT

A method for the measurement of ambient levels of ethylene dichloride (EDC) was developed and field tested. A 24-hour integrated sample is taken with an activated charcoal tube, followed by desorption of the EDC with carbon disulfide. The carbon disulfide solution is then analyzed for EDC by separation on a gas chromatograph and detection with a mass spectrometer. Development of the method included the following area steps:

- Selection of gas chromatographic conditions and a detection system for separation and quantification of EDC.
- Determination of adsorption capacity of the charcoal tube for EDC.
- Evaluation of the desorption of EDC from adsorbents under dry and wet conditions.
- Evaluation of optimum sampling rates.
- Determination of total method efficiency.
- Evaluation of the method under field conditions by use of data from field studies.

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ABSTRACT

A procedure was developed and tested to measure ambient levels of ethylene dichloride (EDC). An activated charcoal tube was employed to collect a 24-hour integrated sample which was subsequently desorbed of ethylene dichloride using carbon disulfide. The carbon disulfide solution was then analyzed for ethylene dichloride by gas chromatography (GC) separation combined with detection by mass spectrometry (MS). Developmental methods included the following steps:

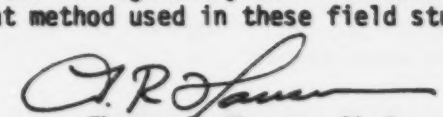
- selection of gas chromatographic conditions and a detection system for separation and quantification of EDC;
- determination of adsorption capacity of the charcoal tube for EDC;
- evaluation of the desorption of EDC from adsorbents under dry and wet conditions;
- evaluation of optimum sampling rates;
- determination of total method efficiency; and
- evaluation of the method under field conditions by use of field study data.

This report was submitted in fulfillment of Contract No. 68-02-2722, assignments No. 7 and No. 12 by PEDCo Environmental, Inc. under the sponsorship of the Environmental Protection Agency. This report covers the period August 1, 1978, to March 1, 1979, and work was completed as of May 1, 1979.

FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina has responsibility for: assessment of environmental monitoring technology and systems; implementation of agency-wide quality assurance programs for air poliution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air, Noise and Radiation, the Office of Toxic Substances and the Office of Enforcement.

A system for measurement of ethylene dichloride in ambient air was developed and evaluated for use in fenceline monitoring. Field studies were conducted and data was reported by use of this measurement system. Data on ethylene dichloride in ambient air was requested by the Office of Air, Noise and Radiation of EPA for their use in regulatory decision-making. This report documents the measurement method used in these field studies.



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SECTION 1

INTRODUCTION

In 1964, Otterson and Guy described a technique for monitoring workplace air for toxic organic vapors (1). They sampled the air with "homemade" tubes filled with activated charcoal; removed the organics with a solvent; and analyzed the resulting solution by gas chromatography. Since passage of the Occupational Safety and Health Act of 1970, researchers have studied the possibility of using many solid sorbents in the sampling of toxic vapors. Work by the National Institute for Occupational Safety and Health (NIOSH), in conjunction with private researchers and commercial companies, has led to the commercial availability of charcoal tubes exhibiting only minor variability and which are simple and inexpensive to use (Figure 1). The standard 7-cm tube contains a 100-mg primary section and a 50-mg backup section to detect breakthrough.

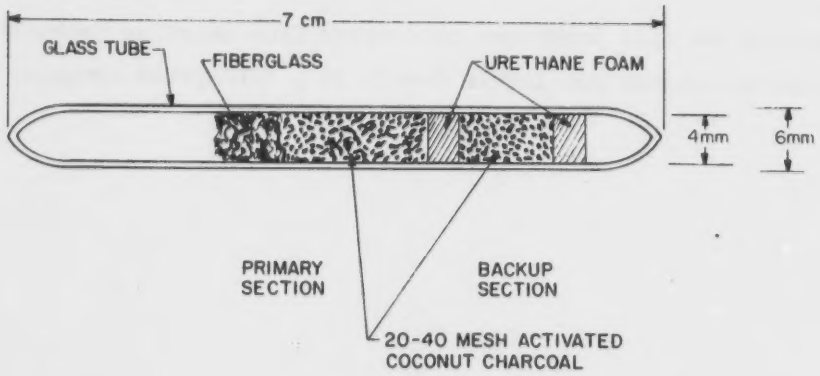

Figure 1. Diagram of a 150-mg charcoal tube.

Both the U.S. Environmental Protection Agency (EPA) and the Occupational Safety and Health Administration (OSHA) have recently emphasized the carcinogenic potential of exposure to ethylene dichloride (EDC). As a result, considerable work has been done on EDC sampling with charcoal tubes. Documentation

of OSHA methods for EDC sampling (2,3) includes information on the behavior of EDC on charcoal. Samples were generated to determine the breakthrough volume and desorption efficiencies for EDC at various concentrations (0.5, 1, and 2 times the threshold limit of 100 ppm). Tests run at a sampling rate of 187 cm^3/min with an EDC concentration of 821 mg/m^3 (≈200 ppm) for 2.5 h showed a 5 percent breakthrough of EDC to the backup section. NIOSH reports that the desorption efficiency with carbon disulfide is approximately 95 percent. Likewise, the migration of sample through the tube is essentially zero.

Recent work by Saalwechter, et al. (4) demonstrated that sampling efficiency on charcoal is reduced in the presence of high humidity because water molecules take up available receptor sites.

Other techniques employing large stainless steel tubes packed with gas chromatographic substrates such as Tenax have been used for collection of organic materials. Tenax, however, has some shortcomings with respect to the collection of low-molecular-weight compounds and also with respect to water adsorption. Tenax has been widely used in qualitative analyses in which thermal desorption is followed by cryogenic concentration; gas chromatographic separation; and mass spectrometer identification (15).

The purpose of this study was to develop from existing technology a method for quantitating ambient EDC levels over a 24-h integrated sampling period.

SECTION 2

CONCLUSIONS

A literature search resulted in the development of a monitoring system which was subsequently subjected to a laboratory examination and a field monitoring program. Data from the latter study were then evaluated to determine the applicability of the method.

The procedure was based on adsorbing EDC on charcoal at a sampling rate of 65 cm^3/min for a 24-h period. Analysis consisted of desorption of EDC from charcoal, and its separation and detection by gas chromatography and mass spectrometry (GC-MS).

Laboratory evaluations indicated an overall method efficiency (accuracy) of approximately 90 percent when tested within an EDC concentration range of 2.5 to 126 $\mu g/m^3$ (0.6 to 31 ppb). The precision of the laboratory tests, based on statistical analyses (relative standard deviation) of replicate standard solutions, was 3 percent. No estimate can be made of its accuracy under field conditions. Analyses of "blind" check samples of EDC on charcoal tubes indicated a total recovery of 70 ±20 percent. Precision of the method under field conditions based on statistical analyses of duplicate (collocated) samples was 6 percent.

SECTION 3

METHOD EVALUATION

SELECTION OF EDC DETECTION METHOD

Gas chromatography was selected for quantitation of EDC because of its selectivity, reproducibility, and relatively short analysis time requirement. Various detectors were examined and compared to determine which would give the best blend of selectivity, sensitivity, and reproducibility. Flame ionization was quickly discarded because its lower limit of reproducible detection was approximately 20 ng (injected on column). Electron capture detection offered a tremendous increase in sensitivity (down to 50 pg injected), but interferences from the desorbing solvent (carbon disulfide) precluded its use as the detector.

In evaluating mass spectrometry, EDC was detected by monitoring selected masses that, although not unique to EDC, were unlikely to be affected by interference from other compounds. In monitoring masses at 62, 98, 100, and 102 m/e, which are all characteristic of EDC, quantitation was performed with the certainty that this compound was EDC and not some other coeluting contaminant. In addition, the multiple ion detection (MID) technique gave a sensitivity to approximately 3 ng for column injection. This method presented the best blend of sensitivity and selectivity and was therefore selected for the EDC analyses.

GC-MS Methodology

Selective ion monitoring (SIM) or multiple ion detection (MID) are two names given the mass spectrometric technique employed to quantitate EDC in carbon disulfide solutions. It is based on the ionization of a compound to fragments of certain masses unique to that compound. The abundance of these fragment

masses is directly proportional to the amount of compound injected.

For EDC, four masses at 62, 98, 100, and 102 m/e were selected. The abundance of mass 62 quantitates the amount of EDC present; the other three masses are used to confirm that the peak measured is EDC. The mass spectrometer plots a curve of the integration units obtained from mass 62 against time. The area under this curve at the retention time expected for EDC is used in the quantitation.

Analysis of several standards on our GC-MS (Hewlett-Packard model 5992-A) indicated that responses to identical concentrations of injected EDC varied from hour to hour, and more substantially from day to day. To alleviate this problem, an internal standard was added to each sample before GC-MS analysis. The compound 1-bromohexane was selected because of its favorable retention time and its unlikely appearance in ambient air samples. An important fragment mass of 1-bromohexane, 57 m/e, was monitored for each sample and the area was determined. The area obtained for EDC was divided by the area obtained for 1-bromohexane to yield a response ratio. (Although the responses to EDC and 1-bromohexane may change over time, the ratio is expected to remain constant.) The response ratio obtained from standards was then used to determine the amount of EDC in unknowns by use of the following equation:

$$W_{EDC} = \frac{(R_{spl} - R_{blk})}{R_{std}} \; CV \qquad \text{(Eq. 1)}$$

where W_{EDC} = weight EDC, ng

$R_{spl} = \frac{\text{area EDC peak}}{\text{area 1-bromohexane peak (from sample)}}$

$R_{blk} = \frac{\text{area EDC peak}}{\text{area 1-bromohexane peak (from blank)}}$

$R_{std} = \frac{\text{area EDC peak}}{\text{area 1-bromohexane peak (from standard)}}$

C = concentration of standard, ng/µl

V = volume of carbon disulfide and 1-bromohexane desorbing solution used to desorb the charcoal tube; normally constant at 750 µl

Gas Chromatographic Conditions

Separation of EDC was done on a nickel column 6.1 m long with an inner diameter (i.d.) of 2.0 mm containing 10 percent SP 1000 on 80/100 mesh Supelcoport (wt/wt). Operating conditions were selected so that EDC was separated from carbon disulfide solvent before injection of the sample stream into the mass spectrometer. Typical operating conditions for analyses of EDC by SIM on a Hewlett-Packard 5992-A analyzer were as follows:

- helium — 0.45 atm
- injector temperature — 170°C
- oven temperature — 120°C isothermal
- solvent elution time — 5.3 min
- run time — 12.5 min
- electron multiplier voltage — indicated by autotune
- ion masses for EDC — 62, 49, 98, 100, and 102 m/e
- ion masses for 1-bromohexane — 57, 85 m/e
- dwell times — 750.0 ms for 62, 49, 57, 85 m/e; 500.0 ms for 98, 100, and 102 m/e
- selective ion monitoring window sizes — 0.10 m/e
- amount of carbon disulfide injected — 4 µl
- retention time of EDC — 6.4 min
- retention time of 1-bromohexane — 9.0 min

INITIAL DETERMINATION OF ADSORPTION CAPACITY OF EDC ON CHARCOAL

NIOSH has demonstrated that the 100-mg front portion of the charcoal tube will hold more than 23 mg of EDC with minimal breakthrough (less than 5%) (3). Tests were conducted with an EDC concentration of approximately 200 ppm over a period of 2.5 h. Because of this high capacity of charcoal for EDC, additional confirmation tests were omitted.

DETERMINATION OF EDC DESORPTION EFFICIENCY FROM CHARCOAL

Desorption of EDC from Dry Charcoal

Charcoal tubes from a supplier were injected with 41.3 µg EDC via a microliter syringe and then refrigerated at 0°C for 24 h before desorption and analysis. Desorption consisted of removing the front and back sections of the tube and placing them in separate 3-ml reaction vessels. The vials were sealed with Teflon-coated serum liners and screw caps; 0.5 ml of cold carbon disulfide was injected into each vial; and the samples were placed in an ultrasonic ice bath for 30 min. After desorption, samples were analyzed for EDC by GC-MS. Data from this test series are presented in Table 1. Average desorption efficiency was 94 ± σ 6 percent. EDC was not detected in the back section of the tubes, an indication that migration to the back did not occur.

TABLE 1. DESORPTION EFFICIENCY OF EDC FROM DRY CHARCOAL

EDC injected, µg	EDC recovered, µg	Desorption efficiency, %
41.3	35.8	86.7
41.3	34.8	84.3
41.3	40.5	98.1
41.3	41.3	100.0
41.3	38.5	93.2
41.3	41.0	99.4
41.3	39.8	96.3
0	N.D.*	

*N.D. - nondetectable

Desorption of EDC from Humidified Charcoal

Charcoal tubes were humidified with an air stream of 99+ percent relative humidity at a rate of 200 cm^3/min for 24 h. After humidification the tubes were injected with 41.3 µg EDC and desorbed. The results of this test (Table

2) demonstrated that humidification of the charcoal slightly reduced the desorption efficiency, which averaged 84 ± σ 14 percent. From these desorption efficiency tests, adsorption of EDC under dynamic conditions was evaluated.

TABLE 2. DESORPTION EFFICIENCY OF EDC FROM HUMIDIFIED CHARCOAL

EDC injected, µg	EDC recovered, µg	Desorption efficiency, %
41.3	35.7	86.5
41.3	24.8	60.0
41.3	33.5	81.0
41.3	33.1	80.0
41.3	46.0	111.3
41.3	31.7	76.6
41.3	36.9	89.3
41.3	35.4	85.7
0	N.D.*	

*N.D. - nondetectable

EDC ADSORPTION EFFICIENCY TESTS

A device was fabricated to generate test atmospheres for the dynamic adsorption tests (Figure 2). The system consisted of a regulated clean air source (room air); bubblers to humidify the air stream; and apparatus to control the temperature and moisture content of the gas stream. EDC under pressure (in cylinders) was used, at concentrations certified by the supplier to ±2 percent. EDC was then diluted with humidified air to achieve the concentration ranges anticipated in ambient atmospheres. A water-jacketed manifold was employed to distribute the gas mixture to the charcoal tubes. Sampling rates through the tubes were controlled by means of critical-flow orifices and a vacuum source activated by a timer. Actual test periods were recorded with a time meter. Testing apparatus was operated in a small laboratory module held 2 to 3°C above the temperature of each test, to eliminate possible condensation on the inlet to the water-jacketed manifold. The temperature of the test mixture was measured with a total immersion thermometer placed inside the manifold.

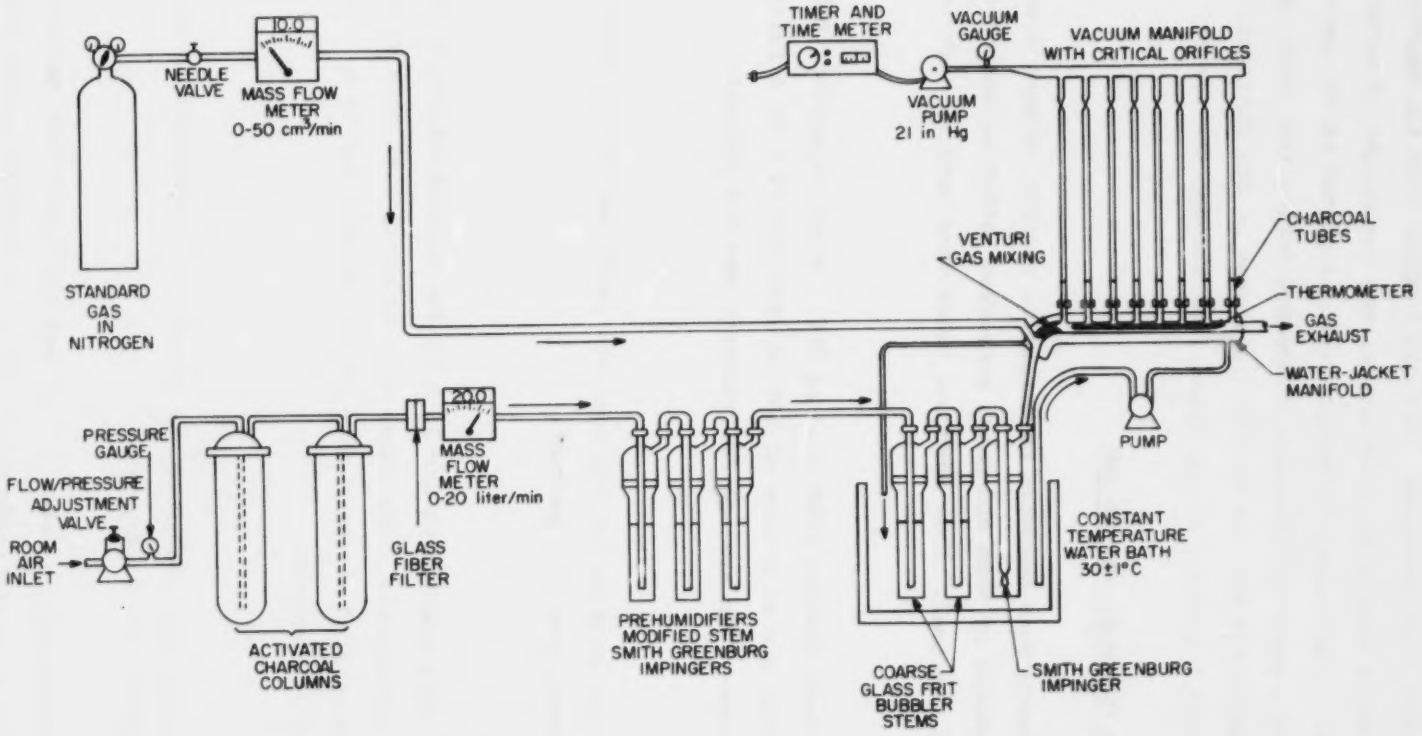

Figure 2. Apparatus for adsorption tests at high humidity.

Preliminary tests were conducted to determine the degree of relative humidity that the apparatus could generate. Gas was sampled from the manifold through a known weight of magnesium perchlorate, and the weight of water collected was determined. The relative humidity was calculated as 99+ percent. Relative humidity tests were not routinely conducted during test runs, provided that the standard compressed EDC gas mixture (prepared in dry nitrogen) was maintained at less than 1 percent of the total flow through the system.

Evaluation of EDC on Charcoal and XE-340

Four separate tests were executed to determine whether carbonaceous sorbent XE-340, manufactured by Rohm and Haas, possessed better sorbent characteristics than those of charcoal. Four sorption tubes were used in each test.

Dry Charcoal--

Charcoal tubes were charged with 41.3 µg EDC. After injection, tubes were subjected to humidified air at a rate of 500 cm^3/min for 24 h at a relative humidity of 99+ percent. The average EDC recovery was 9.8 percent.

Dry XE-340--

The same procedure used on dry charcoal was performed on dry resin XE-340. The average EDC recovery was 25.8 percent.

Wet Charcoal--

Charcoal tubes were humidified for 24 h at 99+ percent relative humidity and a flow rate of 500 cm^3/min. The tubes were injected with 41.3 µg EDC and then subjected to humidified air at a rate of 500 cm^3/min for 24 h. The average EDC recovery was 7.7 percent.

Wet XE-340--

The humidification test procedure was applied to prehumidified XE-340 tubes. The average EDC recovery was 23.4 percent.

The data are summarized in Table 3. It was concluded that carbonaceous sorbent XE-340 offers more desirable qualities as a sorption medium than charcoal.

Tests were discontinued with XE-340 because the material was not commercially available in sufficient quantities to continue the evaluation.

TABLE 3. EVALUATION OF CHARCOAL AND XE-340

Test condition	EDC injected, µg	EDC found, µg		EDC recovered, %
		Front half	Back half	
Dry charcoal	41.3	3.3 ± 0.4	1.5 ± 0.7	9.8
Wet charcoal	41.3	2.1 ± 1.0	1.0 ± 0.1	7.7
Dry XE-340	41.3	9.7 ± 1.7	1.0 ± 0.5	25.8
Wet XE-340	41.3	7.6 ± 0.5	2.0 ± 0.1	23.4

METHOD EVALUATION TESTS

Tests at High Humidity and Temperature

Several test series were conducted with the apparatus shown in Figure 2. The sampling period was 24 h, relative humidity was 99+ percent, and gas temperature was 30°C. Sampling rates and EDC concentrations were varied in order to obtain data indicating the highest EDC recovery without sacrificing sensitivity.

Evaluation of a 500 cm^3/min Sampling Rate with 139 µg/m (34 ppb) EDC--

Charcoal tubes injected with EDC at a concentration of 139 $\mu g/m^3$ were placed on the apparatus, and sampling was conducted for 24 h. Samples were desorbed and analyzed by GC-MS. The results presented in Table 4 show that approximately 84 percent of the EDC passed through both halves of the charcoal tube. The average recovery was 16 percent; 6 percent was found on the back half of the tube. Stemming from these results, lower sampling rates were investigated in later studies.

Evaluation of a 150-cm^3/min Sampling Rate with 126 $\mu g/m^3$ (30 ppb) EDC--

Tests were conducted at a sampling rate of 150 cm^3/min and an EDC concentration of 126 $\mu g/m^3$. Average EDC recovery was 58 percent (Table 5). EDC was detected in the back and front halves of the tube.

TABLE 4. EVALUATION AT A SAMPLING RATE OF 500 cm^3/min AND 139 $\mu g/m^3$ EDC AT HIGH HUMIDITY

EDC sampled, µg	EDC found, µg		EDC recovered, %
	Front half	Back half	
115.3	13.7	7.1	18.0
99.4	10.2	6.2	17.0
113.8	12.8	6.5	16.9
118.1	9.5	4.8	12.0
118.1	11.7	6.3	15.2
115.3	10.9	7.1	15.6
99.4	11.7	7.2	19.0
0	N.D.*	N.D.	

*N.D. - nondetectable

TABLE 5. EVALUATION AT A SAMPLING RATE OF 150 cm^3/min AND 126 $\mu g/m^3$ EDC AT HIGH HUMIDITY

EDC sampled, µg	EDC found, µg		EDC recovered, %
	Front half	Back half	
29.09	12.5	4.5	58.3
29.09	10.8	4.8	53.3
28.67	12.4	4.8	60.1
28.62	12.0	5.1	59.7
0	N.D.*	N.D.	

*N.D. - nondetectable

Evaluation of a 65 cm^3/min Sampling Rate with 126 $\mu g/m^3$ (30 ppb) EDC--

Additional tests were run at a sampling rate of 65 cm^3/min and an EDC concentration of 126 $\mu g/m^3$. Average EDC recovery was 92 percent (Table 6). Less than 5 percent of the EDC was found in the back half of the charcoal tube.

Evaluation of a 65 cm^3/min Sampling Rate with 14.6 $\mu g/m^3$ (3.65 ppb) EDC--

In tests at a sampling rate of 65 cm^3/min and an EDC concentration of 14.6 $\mu g/m^3$, the average EDC recovery was 91 percent (Table 7). EDC was undetected in the back half of the charcoal tube.

Evaluation of a 65 cm^3/min Sampling Rate With 348 $\mu g/m^3$ (186 ppb) EDC--

At a sampling rate of 65 cm^3/min and an EDC concentration of 348 $\mu g/m^3$ the average EDC recovery was 90 percent (Table 8). Approximately 8 percent of EDC was detected on the back half of the charcoal tube. This breakthrough of EDC could have resulted in losses beyond the back portion of the tube.

Evaluation of a 65 cm^3/min Sampling Rate with 2.5 $\mu g/m^3$ (0.6 ppb) EDC--

For sampling rates of 65 cm^3/min and EDC concentrations of 2.5 $\mu g/m^3$, the average EDC recovery was 80 percent (Table 9). EDC was undetected on the back half of the tube because any EDC present would have been below the GC-MS detection limits.

Tests at Moderate Humidity and Temperature

For tests at moderate humidity, a test atmosphere was generated in which impingers previously employed to saturate the air with water vapor were replaced with a temperature equilibration coil of copper tubing (Figure 3). These tests were performed at 25°C and a relative humidity of 64 percent (the prevailing relative humidity of the air within the laboratory facility).

Evaluation of 65 cm^3/min Sampling Rate with 2.7 $\mu g/m^3$ (0.6 ppb) EDC--

A test series was conducted for 24 h at a temperature of 25°C and relative humidity of 64 percent. The front portion of the charcoal tube contained 79 percent of the EDC, the average recovery value. The back portion was analyzed, but any EDC present would have been below the GC-MS detection limit. The data are given in Table 10.

TABLE 6. EVALUATION AT A SAMPLING RATE OF 65 cm^3/min AND 126 $\mu g/m^3$ EDC AT HIGH HUMIDITY

EDC sampled, µg	EDC found, µg		EDC recovered, %
	Front half	Back half	
11.54	10.0	0.5	90.9
12.20	10.0	N.D.	86.0
13.33	12.2	0.6	96.0
12.30	11.2	0.5	95.0
0	N.D.*	N.D.	

*N.D. - nondetectable

TABLE 7. EVALUATION OF A SAMPLING RATE OF 65 cm^3/min AND 14.6 $\mu g/m^3$ EDC AT HIGH HUMIDITY

EDC sampled, µg	EDC found, µg	EDC recovered, %
1.56	1.54	98.7
1.35	1 17	86.7
1.38	1.32	95.6
1.45	1.37	94.7
1.60	1.23	77.0
1.39	1.27	91.4
0	N.D.*	

*N.D. - nondetectable

TABLE 8. EVALUATION AT A SAMPLING RATE OF 65 cm^3/min AND 348 $\mu g/m^3$ EDC AT HIGH HUMIDITY

EDC sampled, µg	EDC found, µg		EDC recovery, %
	Front half	Back half	
37.70	30.58	2.31	87
32.20	20.63	1.77	91
32.00	26.91	1.22	88
32.46	28.61	1.02	91
33.71	28.08	2.42	90
37.21	31.40	3.74	94
33.21	27.85	2.99	93
33.71	26.25	3.51	88
0	N.D.*	N.D.	

*N.D. - nondetectable

TABLE 9. EVALUATION AT A SAMPLING RATE OF 65 cm^3/min AND 2.5 $\mu g/m^3$ EDC AT HIGH HUMIDITY

EDC sampled, µg	EDC found, µg	EDC recovered, %
0.24	0.19	79
0.23	0.20	84
0.25	0.21	82
0.23	0.17	75
0.23	0.18	76
0.24	0.21	84
0.24	0.19	80
0	N.D.*	

*N.D. - nondetectable

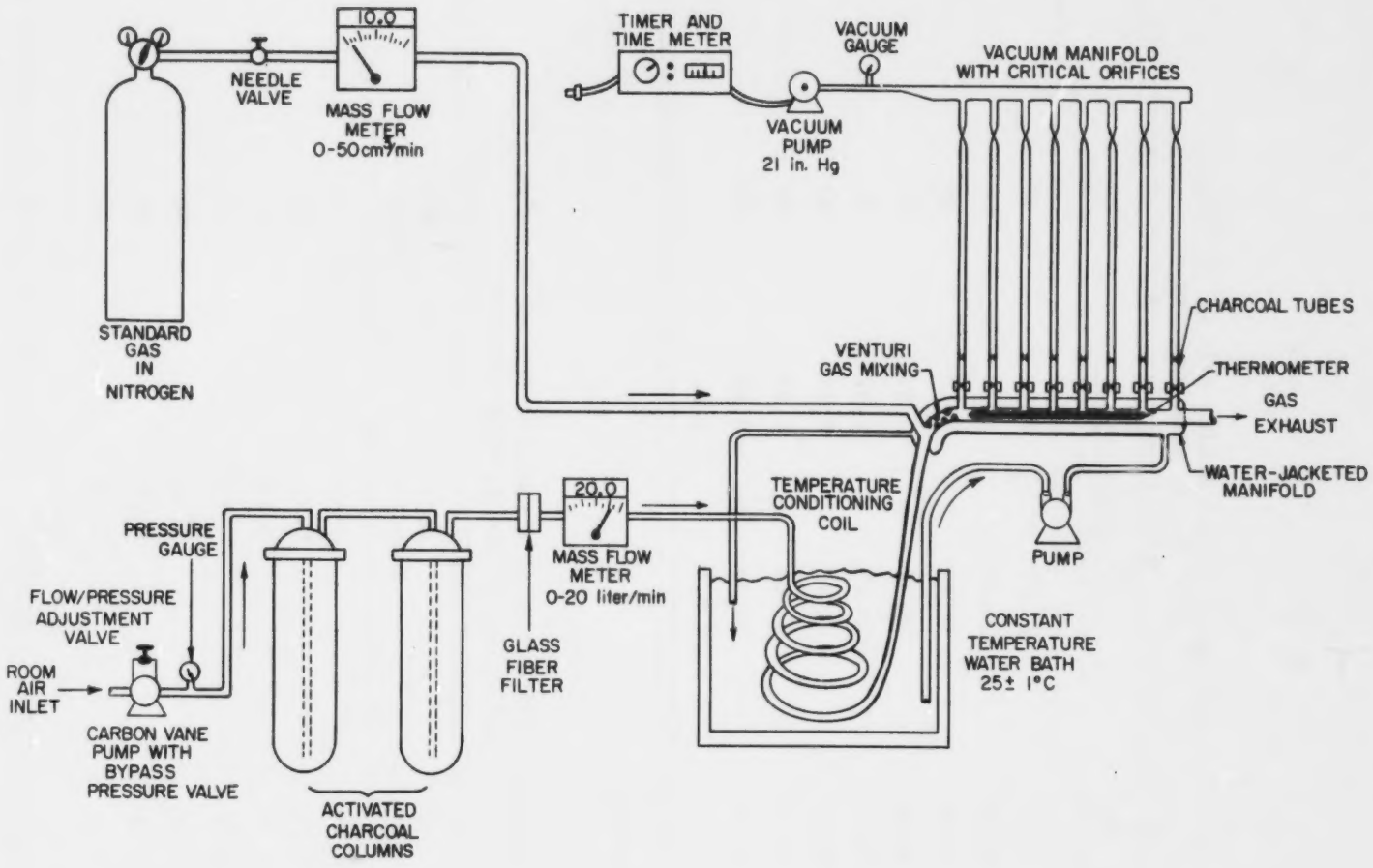

Figure 3. Apparatus for adsorption tests at moderate humidity.

TABLE 10. EVALUATION AT A SAMPLING RATE OF 65 cm^3/min AND 2.7 $\mu g/m^3$ EDC AT MODERATE HUMIDITY

EDC sampled, µg	EDC found, µg	EDC recovery, %
0.24	0.18	77
0.25	0.22	85
0.26	0.22	82
0.24	0.18	73
0.27	0.20	75
0.25	0.20	81
0.24	0.20	80
0	N.D.*	

*N.D. - nondetectable

TABLE 11. EVALUATION AT A SAMPLING RATE OF 65 cm^3/min AND 36 $\mu g/m^3$ EDC AT MODERATE HUMIDITY

EDC sampled, µg	EDC found, µg	EDC recovered, %
3.37	2.97	88
3.47	2.98	86
3.63	3.01	83
3.27	2.94	90
3.21	2.95	92
3.32	2.95	89
3.37	2.97	88
0	N.D.*	

*N.D. - nondetectable

Evaluation of 65 cm^3/min Sampling Rate with 36 $\mu g/m^3$ (9 ppb) EDC--

At a sampling rate of 65 cm^3/min, an EDC concentration of 36 $\mu g/m^3$, and 64 percent humidity, the average EDC recovery was 88 percent (Table 11). No EDC was detected on the back half of the tube.

SUMMARY OF LABORATORY EVALUATIONS

Dry charcoal was found to have a high affinity for EDC. However, the presence of water markedly decreased this quality. Although the carbonaceous sorbent XE-340 was found superior to charcoal for EDC collection, the limited supply of this material terminated any further evaluation of this method.

Dynamic tests at various EDC levels under conditions of high temperatures and humidity (30°C, 99+ relative humidity) for 24-h sampling periods revealed significant EDC breakthroughs in the charcoal tubes for sampling rates above 65 cm^3/min. These experiments yielded an overall average recovery above 90 percent for EDC levels ranging from 2.5 to 126 $\mu g/m^3$ (0.6 and 31 ppb). For EDC concentrations of 348 $\mu g/m^3$ (86 ppb), a breakthrough of approximately 10 percent was observed.

As a result of these studies, a configuration employing two tubes was designed to ensure against the EDC breakthrough which occurred during single tube sampling. This tandem tube configuration (Figure 4) was incorporated into the EDC Method described in Appendix A, and was used in all field monitoring studies. The first tube was used as the front portion, and the second tube was used as the back portion.

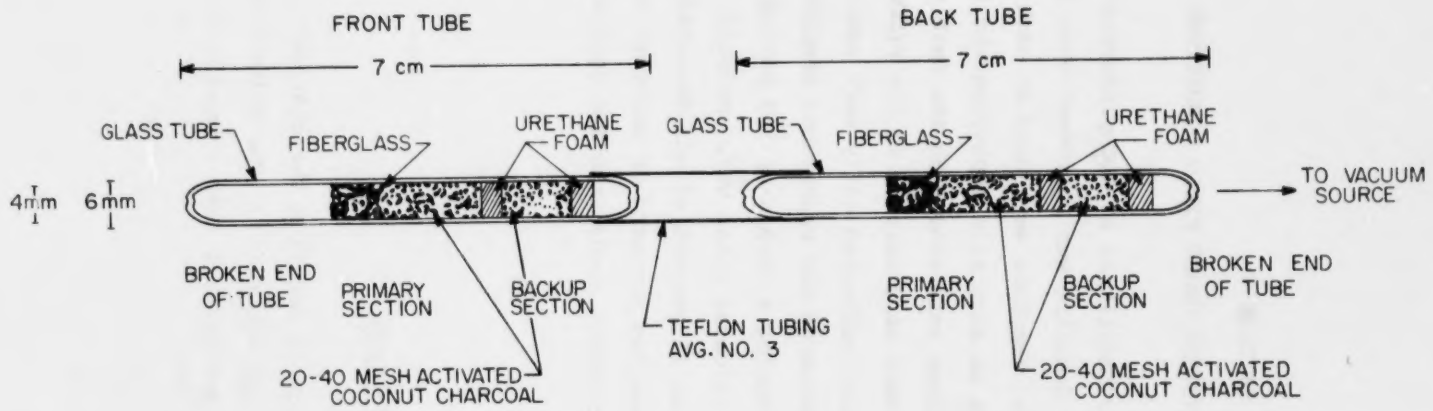

Figure 4. Diagram of tandem charcoal tubes (with broken ends) for EDC sampling.

SECTION 4

EVALUATION OF EDC METHOD UNDER FIELD CONDITIONS

A study was conducted near the facilities of EDC producers and users to determine ambient EDC levels (6). Sampling was performed over 24-h sampling periods at 3 sites 10 times. Twelve samplers were used at each site. The sampling was performed in duplicate at each site employing the tandem charcoal tube configuration. All field samples were stored in the dark at 0°C until analyses were performed. Samples were hand carried to the PEDCo laboratory, where 50 to 70 percent of the samples collected daily were analyzed. Selection of samples, including those from downwind and background samplers, was based on the prevailing wind conditions during a 24-h sampling period. Ten percent of the duplicate samples from the selected sites were analyzed. In addition, replicate analyses were performed on 10 percent of all desorbed samples. Internal standard solutions, check samples prepared on charcoal tubes, and blanks were also analyzed. For this particulate study, the EDC method was followed as described in Appendix A.

MATERIALS AND STANDARDS

Purity Check of Carbon Disulfide Solvent

The solvent used for desorption of EDC from the charcoal tubes was Fisher Reagent Quality carbon disulfide (Lot No. C184). The solvent was analyzed by GC-MS more than 30 times (several analyses of each opened bottle), and no EDC was detected.

Purity Check of Charcoal Tubes

More than 30 unused 150-mg charcoal tubes manufactured by the SKC Corporation (Pittsburgh, Pennsylvania: Lot No. 107) were analyzed by GC-MS during field sample evaluation. No EDC was detected.

Purity Check of EDC Standard Reference Material

Ethylene dichloride standard solutions were prepared with EDC supplied by Chem Services (West Chester, Pennsylvania; Lot No. 0-642). The manufacturer's quoted purity was 99+ percent. A GC-MS analysis of this material under the identical conditions used during field sample analysis showed no contamination from other compounds. The manufacturer's assay of 99+ percent was therefore assumed accurate. No corrections were made with respect to the purity of this reagent when used in preparing external standard solutions.

EDC BREAKTHROUGH IN SAMPLING OF HIGH LEVELS OF EDC

Although laboratory studies excluded breakthrough tests at extremely high EDC levels, high levels were observed during one of the field studies. To detect a breakthrough, PEDCo analyzed the second (rear) 150-mg charcoal tube for the presence of EDC. Several sets of tubes were selected for analysis, and EDC was detected in the backup tubes twice. Breakthrough occurred only in the EDC range of 200 to 600 $\mu g/m^3$ (60 to 180 ppb) and amounted to about 1 percent. Because breakthrough was undetected in all samples analyzed in that range, it could have resulted from nonhomogeneous packing of the charcoal within some of the tubes.

ADSORPTION OF EDC FROM THE AMBIENT ATMOSPHERE ON CHARCOAL TUBES UNDER STATIC CONDITIONS

During the three field studies, about 60 charcoal tubes were exposed with one end open to the ambient air for a period of 24 h. This test was to determine whether EDC migrated into a tube before or after dynamic sampling began. Over 20 tubes selected at random from the 3 study sites were analyzed by GC-MS. No EDC was detected.

PRECISION UNDER FIELD CONDITIONS

Analyses of Duplicate (Collocated) Samples

All sampling was performed in duplicate. In about 10 percent of the cases, both collocated samples were analyzed and the resultant data subjected to further statistical analysis to establish the total sampling and analytical error.

Statistical analyses demonstrated that the standard deviation of EDC concentrations increased as EDC increased. The relationship between standard deviation and mean EDC concentration is depicted in Figure 5.

Because of the apparent relationship between the standard deviation and the mean, variability among concentrations (based on collocated sampling) was expressed in terms of relative standard deviation (i.e., $s/\bar{x}$ [100]). Regression analysis supported a relative standard deviation of about 6 percent. This variability measured the precision of both the sampling and analytical procedures.

Duplicate Analysis of Desorbed Field Samples

The relative standard deviation of 6 percent indicated the combined precision of sampling and analysis. To derive an isolated estimate of the precision of the analytical method, duplicate analyses were run on 10 percent of all desorbed samples. The relationship between the mean and standard deviation is depicted in Figure 6. As with the analysis of collocated samples, the standard deviation of the duplicates was proportional to the average concentration. The relative standard deviation (precision) of the analytical method was approximately 3 percent.

Summary of Precision Under Field Conditions

The precision of an individual EDC measurement is approximately 6 percent. This estimate, based on analysis of ambient EDC measurements at the three study sites, includes the precision of both the sampling technique and the analytical method. Precision of the analytical method alone, derived from duplicate analyses of desorbed samples, is approximately 3 percent.

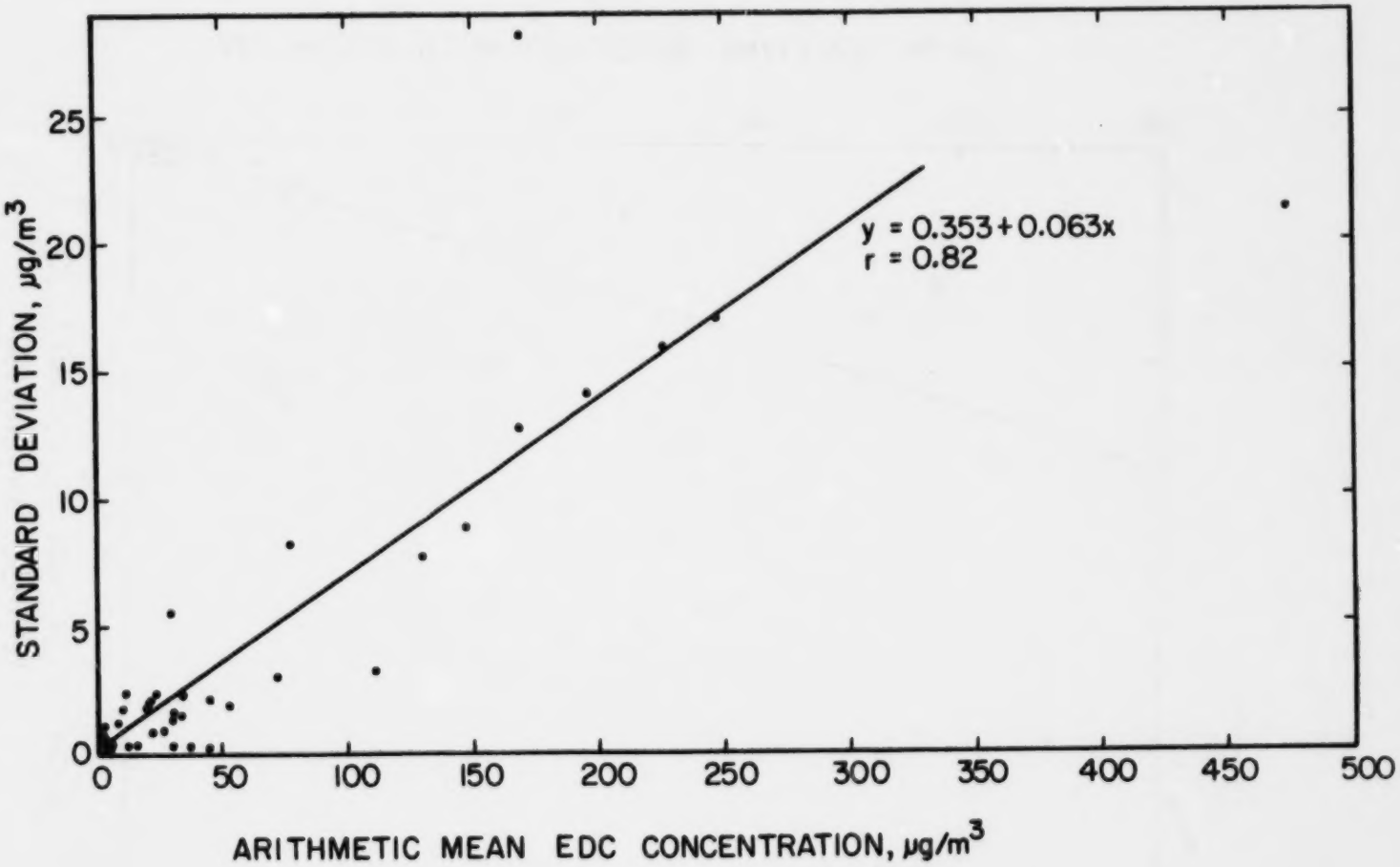

Figure 5. Standard deviation and arithmetic mean concentration of EDC for collocated samples.

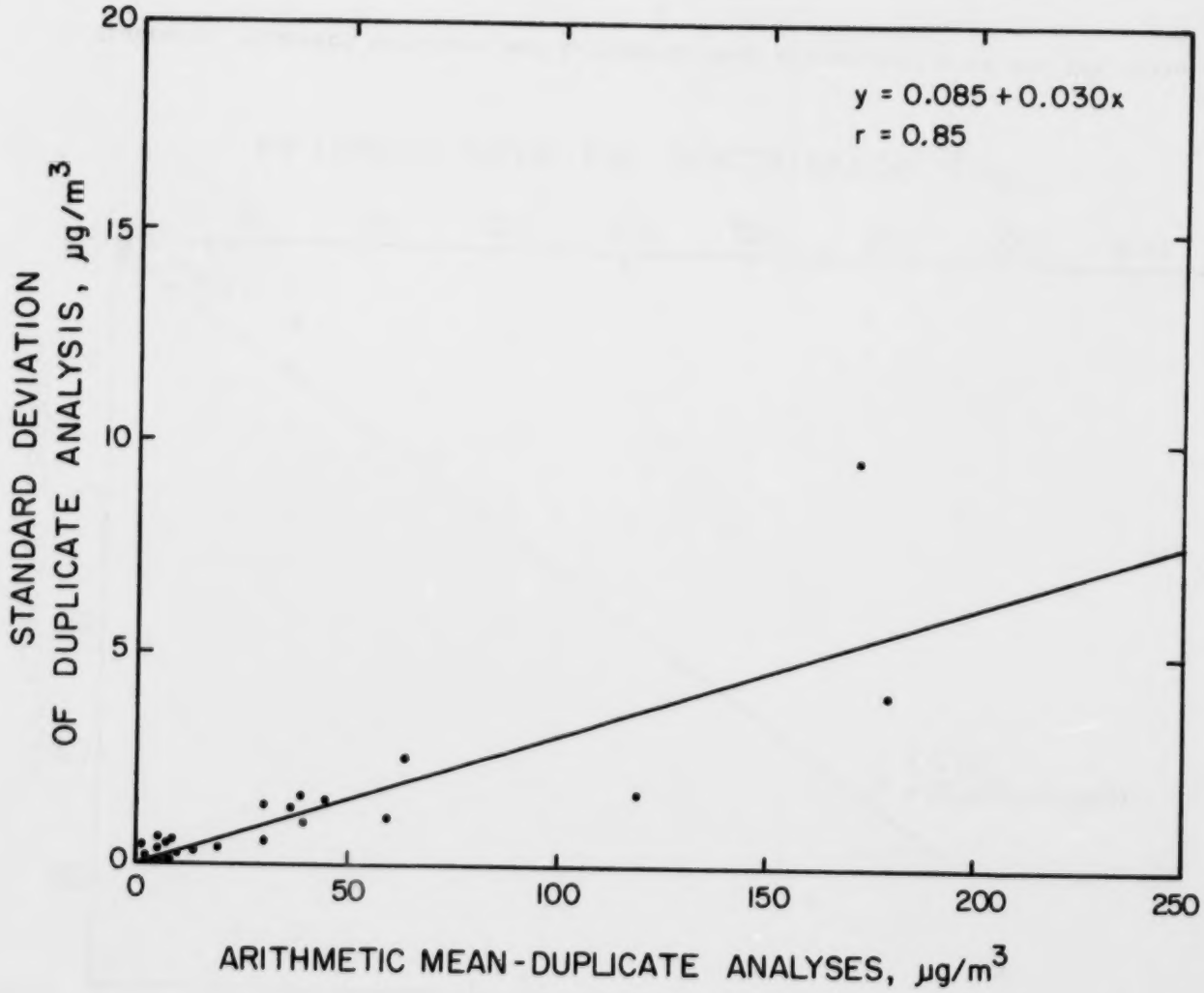

Figure 6. Standard deviation and mean concentration of EDC for duplicate analyses of selected samples.

DETERMINATION OF THE ACCURACY UNDER FIELD CONDITIONS

Analysis of Unknown External Solutions for Quality Control

The GC-MS analyses of field study samples were conducted by several chemists over a period of 2 months. Each chemist prepared standards from a master stock solution and analyzed a batch of 30 to 40 samples. Another chemist, working independently, prepared an external check standard from an independent stock solution of EDC and submitted it to the analyst. The data from this quality control check on the working standard solutions are presented in Table 12.

To develop a relationship between the amount of EDC in the standard solution and that measured by the PEDCo analyst, PEDCo analyzed these data by regression analysis. It was assumed that the precision of adding EDC to the solution was substantially better than EDC determination by GC-MS analysis.

The relationship between the quantity of EDC determined by the GC-MS analysis and that of prepared standard solution can be expressed as:

$$y = 0.12 + 0.97x \qquad \text{(Eq. 2)}$$

where Y = ng/µl EDC determined by the GC-MS
x = ng/µl EDC in the standard solution

Thus, the recovery of EDC from standard solution by the GC-MS procedure ranged from 109 percent at 1 ng/µl to 98 percent at 12 ng/µl.

Check Samples Prepared by EPA

The EPA provided 48 samples having known amounts of EDC ranging from 1.18 to 8.26 µg. These samples were prepared with a gravimetrically calibrated EDC permeation tube and a dilution system. Each charcoal tube was charged with EDC by sampling at a known flow rate of about 65 cm^3/min from the dilution system. By varying the sampling time for each tube, the analyst was able to calculate the amount of EDC adsorbed.

TABLE 12. ANALYSES OF UNKNOWN EXTERNAL STANDARD SOLUTIONS OF EDC*

Date analyzed	EDC concentration, ng/µl	
	Added	Found
10-19-78	1.25	1.50
10-20-78	1.43	1.44
10-20-78	5.04	5.03
10-20-78	3.67	4.40
10-23-78	6.25	5.71
10-23-78	6.25	5.83
10-24-78	1.58	1.69
10-24-78	1.58	1.68
10-24-78	6.25	6.22
10-26-78	3.13	3.26
10-31-78	2.60	2.64
11-10-78	0.78	0.89
11-13-78	0.65	0.50
11-13-78	12.43	12.33
11-14-78	6.28	6.78
11-15-78	3.26	3.21
11-16-78	4.96	4.67
11-17-78	2.71	2.67
11-28-78	6.94	6.65
11-29-78	3.49	3.53
11-30-78	3.14	3.10

*Average 101.3 ± σ 9.6

Table 13 tabulates PEDCo's analysis (by GC-MS) of the 48 EPA check samples. The quantities of EDC found by PEDCo were significantly less than those reported by EPA. For example, in 9 EPA samples reported to contain 1.18 µg EDC, PEDCo found an average of 0.81 µg; a recovery rate of only 69 percent. In 17 samples reported to contain 5.90 µg EDC, PEDCo found an average of 4.64 µg; a recovery rate of 79 percent.

Table 14 shows the standard deviation of replicate analyses for each EDC level added by EPA to its check samples. It is apparent that the standard deviation increased with increasing levels of EDC. Over the various EDC levels added by EPA, the relative standard deviation ranged from 20 to 25 percent.

Check Samples Prepared by PEDCo

PEDCo prepared a set of 16 quality assurance samples, 8 with an EDC level of 4.51 µg and 8 with 9.02 µg. The samples were prepared by using a standard gas mixture of EDC certified by the manufacturer to ±2 percent accuracy and a dilution system. Figure 7 is a diagram of this system, where the two series of check samples were simultaneously prepared. Critical-flow orifices were selected to provide a sampling rate of 65 ±1 cm^3/min. An excess flow of EDC gas mixture was established through the eight-port glass sampling manifold. Eight tubes were connected to critical-flow orifices. Sampling was conducted for 15.0 min to produce low-level check samples and for 30.0 min to produce high-level samples. The amount of EDC absorbed on each tube was then calculated from the EDC concentration as assayed by the supplier and as derived from the sampling rate and time period.

Table 15 presents PEDCo's analysis by GC-MS of these quality assurance samples. For the eight samples prepared at an EDC level of 4.51 µg, the average amount recovered was 4.45 µg a recovery rate of 99 percent. For the 8 samples prepared at 9.02 µg, the average amount recovered was 8.61 µg a recovery rate of 95 percent. Standard deviations (Table 16) were 0.30 µg and 0.27 µg for 4.51 µg and 9.02 µg EDC levels, respectively. There was no significant difference in the standard deviation for either level of EDC.

TABLE 13. QUANTITY OF EDC FOUND IN EPA QUALITY ASSURANCE SAMPLES

AMOUNT OF EDC ADDED BY EPA, µg									
1.18		2.36		3.54		5.90		8.26	
Sample No.	EDC found, µg	Sample No.	EDC found, µg	Sample No.	EDC found, µg	Sample No.	EDC found, µg	Sample No.	EDC found, µg
C	0.53	D	1.37	A	2.62	E	5.45	B	4.47
G	0.66	H	1.27			L	4.67	F	6.75
J	0.89	I	1.50			M	4.84	K	6.07
22	0.89	N	1.13			P	3.56	O	7.49
25	0.64	R	2.07			V	7.47	Q	0.45*
26	1.05	T	1.31			W	3.89	U	6.64
27	0.95	X	1.68			11	4.14	Y	4.81
31	0.99	10	0.94			12	2.72		
33	0.65	13	1.76			16	1.27*		
		14	1.11			18	6.83		
		15	2.14			19	4.90		
		17	1.95			21	2.56		
		20	1.84			23	4.86		
						24	4.85		
						28	4.13		
						29	4.70		
						30	4.51		
						32	4.79		

*Deleted - gross error

TABLE 14. STANDARD DEVIATION OF REPLICATE ANALYSES FOR EDC FOUND IN EPA QUALITY ASSURANCE SAMPLES

	AMOUNT OF EDC ADDED BY EPA, µg				
	1.18	2.36	3.54	5.90	8.26
Mean	0.18	1.54	2.62	4.64	6.04
Std. dev.	0.19	0.39	0	1.22	1.18
Recovery, %	69.00	65.00	74.00	79.00	73.00
Relative std. dev., %	23.00	25.00	0	26.00	20.00

TABLE 15. QUANTITY OF EDC IN PEDCo QUALITY ASSURANCE SAMPLES

AMOUNT OF EDC ADDED BY PEDCo, µg	
4.51 EDC found, µg	9.02 EDC found, µg
4.67	8.29
4.27	8.83
4.12	8.31
4.63	8.72
4.86	8.88
4.71	8.65
4.31	8.28
4.05	8.91

TABLE 16. STANDARD DEVIATION OF PEDCo QUALITY ASSURANCE ANALYSIS

	AMOUNT OF EDC ADDED BY PEDCo, µg	
	4.51	9.02
Mean	4.45	8.61
Std. dev.	0.30	0.27
Recovery, %	99.00	95.00
Relative std. dev., %	6.7	3.1

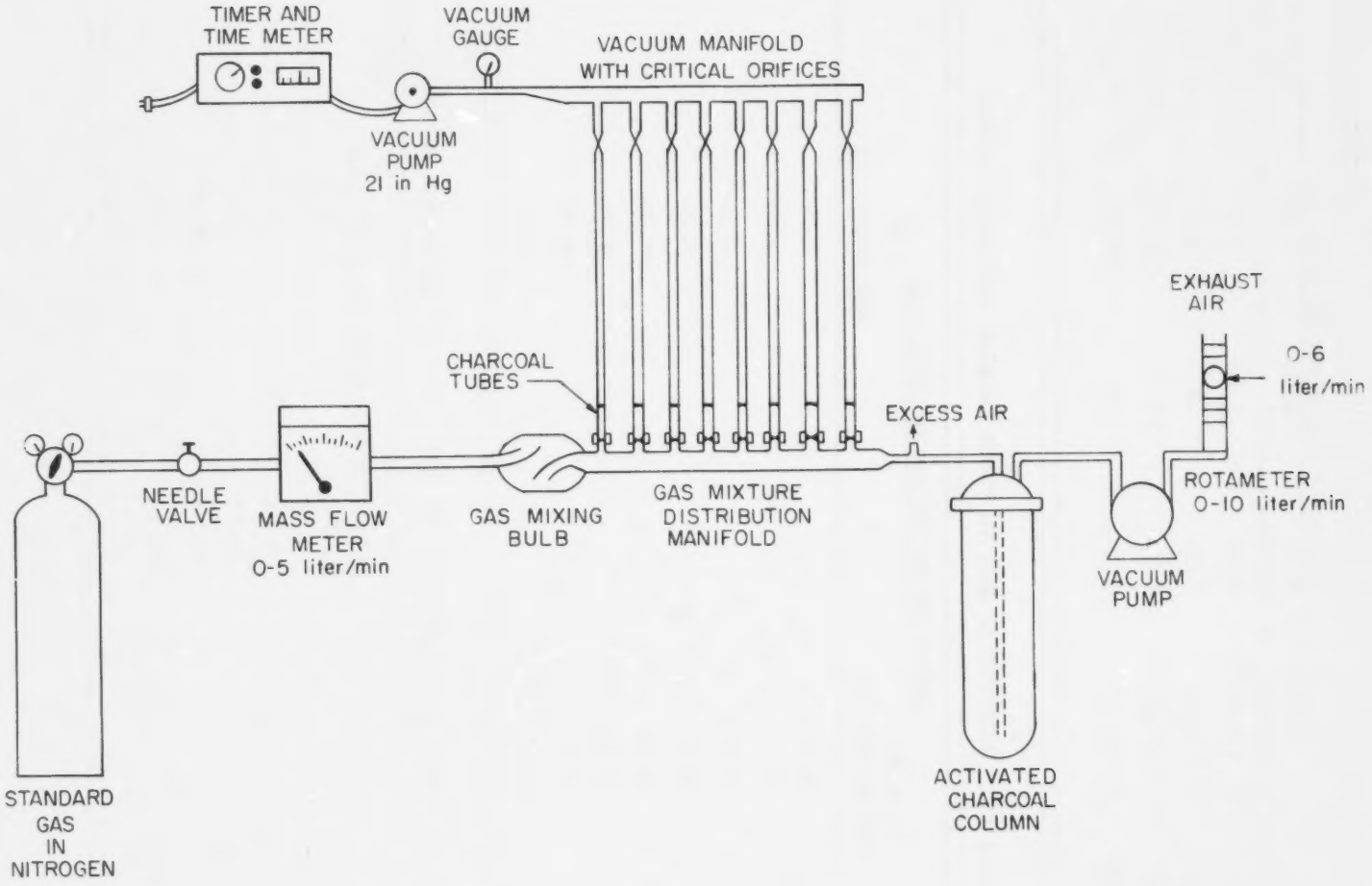

Figure 7. Apparatus for generating and sampling gas mixtures of EDC on charcoal tubes.

Summary of Accuracy Based on Analysis of Check Samples

Analytical results of the two sets of quality assurance samples differed considerably. EDC recovery rates from prepared EPA samples were between 65 and 79 percent. Contrastingly, the rates from samples prepared by PEDCo were 95 and 99 percent. Furthermore, the standard deviation for EPA samples increased as the EDC level increased: from 0.19 µg at the 1.18 µg level to 1.18 µg at the 8.26 µg level. Because the analytical methods were identical, this discrepancy cannot be explained without further investigation.

Since the accuracy of the method cannot be precisely defined, one can only state that the recovery of spiked samples, which is an indication of accuracy, is in the range of 70 ±20 percent.

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APPENDIX A

TENTATIVE METHOD FOR THE DETERMINATION OF ETHYLENE DICHLORIDE IN THE ATMOSPHERE BY 24-HOUR INTEGRATED SAMPLING

This method has been drafted from available information, as presented in the bibliography, and from laboratory and limited field evaluation. It is still under investigation and is subject to revision.

PRINCIPLES OF THE METHOD

A known volume of air is drawn through a charcoal tube for a period of 24 h to trap the ethylene dichloride (EDC) vapors present. The charcoal in the tube is tranferred to a small, stoppered sample container, where it is desorbed with a solvent mixture of carbon disulfide and an internal standard compound (1-bromohexane).* Subsequently, an aliquot of the desorbed sample is injected into a gas chromatograph using a mass spectrometer as the detector. The amount of EDC in the sample is then ascertained by determining the ratio of the peak area for EDC to the peak area for 1-bromohexane and comparing that with the ratio of peak areas obtained from a standard.

RANGE AND SENSITIVITY

The limit of detection is approximately 0.5 $\mu g/m^3$ (0.13 ppb). The maximum of the range is approximately 500 $\mu g/m^3$ (125 ppb); it may be increased by diluting the sample after extraction.

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* Warning: Because EDC is a suspected carcinogen, care must be taken to protect operators from breathing fumes. Carbon disulfide is toxic, and its vapors form explosive mixtures with air; therefore, this material should be handled in a well-ventilated room with a fume hood.

This method was evaluated over an EDC range of 2.5 to 348 $\mu g/m^3$ (0.6 to 86 ppb), at temperatures of 25° and 30°C and relative humidities of 64 and 99+ percent, respectively. The sampling rate was 65 cm^3/min at 760 mm Hg for 24 h. The charcoal adsorption tube (Figure A-1) consisted of two sections of activated charcoal (totalling 150 mg) separated by a section of urethane foam. Each tube was backed with a second tube to determine breakthrough. The laboratory evaluations employed a single charcoal tube and yielded an average total method efficiency (adsorption and desorption) of approximately 90 percent for EDC levels of 2.5 to 126 $\mu g/m^3$ (0.6 to 31 ppb). At concentrations of 348 $\mu g/m^3$ (86 ppb), approximately 10 percent of the EDC was found on the back portion of the tube. At an EDC concentration of approximately 2.5 $\mu g/m^3$ (0.6 ppb), overall method efficiency was approximately 80 percent. The backup tube was analyzed, but its EDC content remained unknown due to GC-MS detection limits.

Although no effect from humidity was observed during the laboratory evaluations at the 65 cm^3/min sampling rate, water condensation within the charcoal tube during field sampling could have affected the adsorption efficiency. Sampling for 24 h at rates in excess of 65 cm^3/min affected the collection efficiency. At an EDC concentration equivalent to 139 $\mu g/m^3$ (34 ppb), tests using a flow rate of 500 cm^3/min and a relative humidity of 99 percent indicated an overall method efficiency of less than 20 percent. For atmospheres suspected of possessing higher levels of EDC and humidity, sampling time should be shortened to less than 24 h.

INTERFERENCES

It is highly unlikely that any common pollutants are present in the ambient atmosphere in concentrations which would interfere with EDC measurements. Several criteria must be met for identification and quantification. Retention time and the specific mass ions of 49, 62, 98, and 100 m/e are simultaneously monitored. These ions should be represented by the identical peak retention time as EDC in order to provide positive EDC quantification. The data system of the spectrometer uses the response of mass ion 62 for quantification.

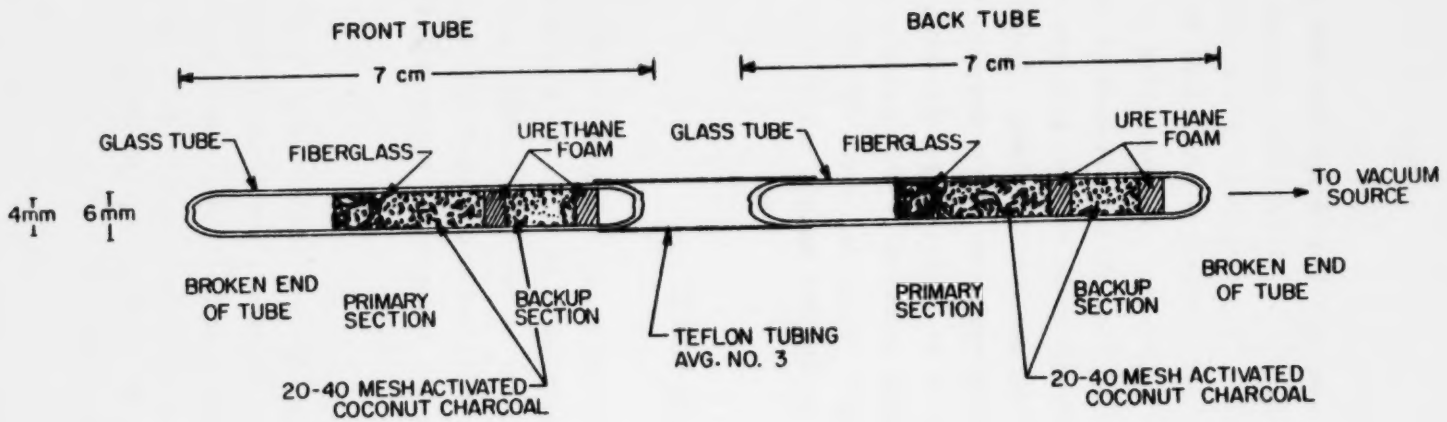

Figure A-1. Diagram of tandem charcoal tubes for EDC sampling.

PRECISION AND ACCURACY

Replicate GC-MS analyses of standard liquid mixtures and sample aliquots must not deviate by more than ±5 percent. Information is presently unavailable on the accuracy of the total method. The precision of the analytical method, based on statistical analysis (relative standard deviation) of replicate standard solutions, was determined as 3 percent. The precision of both the analytical and sampling methods, based on statistical analyses of replicate samples, was determined as 6 percent. Standard check samples prepared by EPA and by PEDCo determined the accuracy of the analytical method. The EPA check samples yielded an average recovery of 72 percent; the PEDCo samples, an average recovery of 97 percent. In an attempt to explain this discrepancy, the possibility of EDC decay on the tube between preparation and analysis was statistically evaluated. No biases were observed. Since an origin for the discrepancy was not ascertained, accuracy of the analytical method can only be estimated as between 72 and 97 percent.

ADVANTAGES AND DISADVANTAGES OF THE METHOD

The sampling device is small, portable, and uses no liquids. Interferences are minimal, and most are eliminated by altering chromatographic conditions. The amount of sample that can be taken is limited by the sampling rate and by tube capacity. When the sample value obtained for the backup tube exceeds 10 percent of that found on the first tube, the possibility of sample loss exists.

A GC-MS system for separation and detection is more costly than a flame ionization detection (FID) system. However, the GC-MS is the only readily available system with the required sensitivity which also provides the maximum criteria that must be met prior to integrating a chromatographic peak. Attempts to use other detection systems (FID, electrolytic conductivity, and electron capture) presented unavoidable problems.

APPARATUS AND MATERIALS

Sample Collection Materials

- pump — capable of maintaining an air pressure differential greater than 0.5 atm at the desired flow rate
- critical orifice — 30-gauge, 0.5-in hypodermic needle to control flow rate at approximately 65 cm^3/min
- filter cartridge — Disposable, 47 mm diameter, 0.45 µm filter porosity (Millipore Filter Corp., Bedford, Massachusetts)
- charcoal adsorption tubes — 150-mg, standard NIOSH type connected in tandem (Figure A-1)
- vacuum gauge — 0-to 760-mm Hg
- airflow meter — rotameter type, 0 to 120 cm^3/min, calibrated against an NBS traceable bubble meter

Sample Recovery Materials

- muffle furnace — for operation at 250°C
- syringe — 0 to 1 ml, gastight with Teflon plunger
- vials — 2-ml capacity
- caps — screw type, with septum hole for 2-ml vials
- serum cap liners — Teflon-coated rubber, for sealing vials and caps
- ultrasonic cleaner — 0.5- to 1-gal capacity (Bronson Cleaning Equipment, Sheldon, Connecticut)

Analytical Equipment

- gas chromatograph with mass spectrometer — Hewlett-Packard 5992-A or equivalent, with glass jet separator and data system
- chromatographic column — nickel, 6.1 m x 2 mm i.d., containing 10 percent SP 1000 on 80/100 Supelcoport

- micro syringes — 0 to 10, 0 to 100, and 0 to 500 µl range
- vials (sample) — 5 ml and 50 ml capacity, with screw caps and Teflon-lined serum cap liners
- pipettes — volumetric Class A, 50 ml, 5 ml, and 1 ml

Reagents

- chromatographic quality carbon disulfide
- 1,2-dichloroethane, reagent grade
- 1-bromohexane, reagent grade
- purified helium

PROCEDURE

Cleaning of Equipment

All glassware employed for laboratory analysis should be washed with detergent, thoroughly rinsed with tapwater and distilled water, dried, and placed in a muffle furnace at 350°C for 30 min to remove trace organic compounds.

Collection of Samples

A tandem arrangement consisting of two 150-mg charcoal tubes is used for sampling; one is identified as the front tube and the other as the backup tube. A 30-gauge, 0.5-in hypodermic needle is installed for critical-orifice flow control. The ends from each tube are removed by breaking off the glass bead. The two tubes are connected with Teflon tubing (5-mm i.d.), directly exposing the large (100-mg) section of charcoal to the sampled air. Tubes are then connected to the sampler, and the pump is activated. Figure A-2 is a schematic diagram of the sampler.

The operator records the initial vacuum, starting time, adsorption tube number, and site location. The sampling rate is measured by connecting a rotameter (calibrated with an NBS traceable bubble meter) to the inlet of a tandem

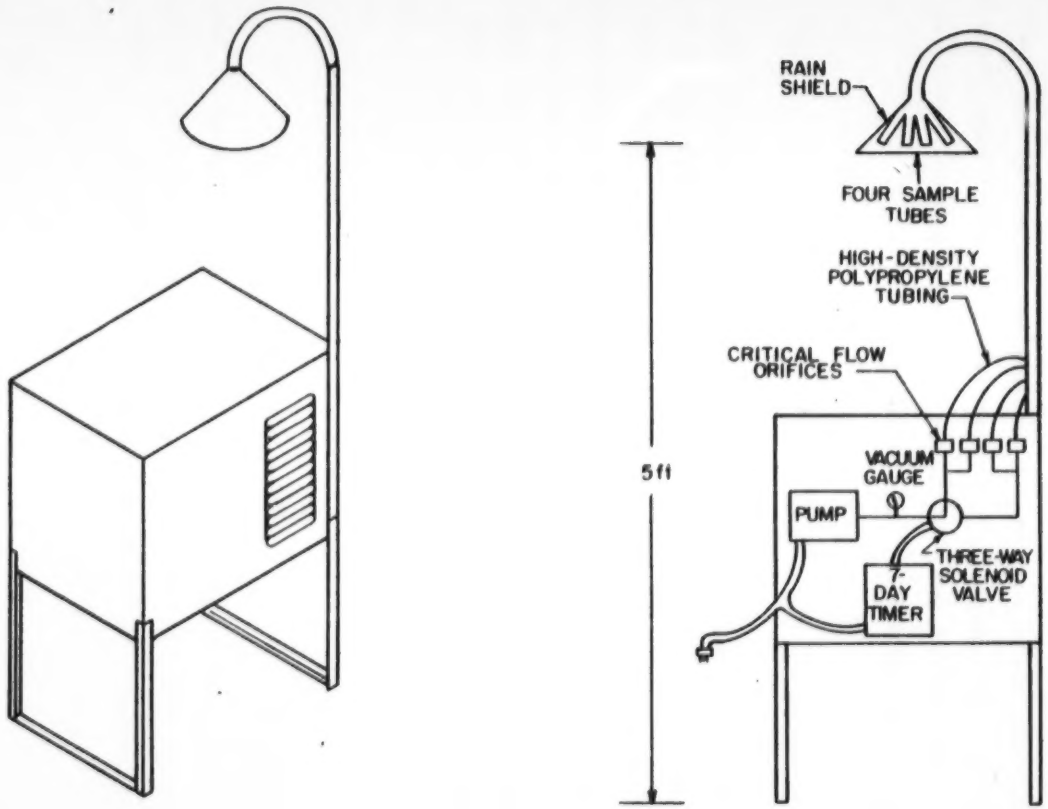

Figure A-2. Sketch of 24-hour integrated sampler for EDC monitoring.

charcoal sampling tube; initial flow is then recorded. A shield is placed over the adsorption tubes to protect them from light and rain, and sampling is continued for 24 ±0.25 h. At the completion of the sampling period, the operator records the time, final vacuum, and flow rate. Samples are then removed from the sampler; plastic caps are placed on the adsorption tubes; the tubes are wrapped in aluminum foil and stored in a freezer at ≤ 0°C until laboratory analyses are performed. One out of every 20 tubes used for field monitoring is retained and returned to the laboratory as a blank.

Sample Recovery

Contents of the 150-mg charcoal tube are transferred into a clean 2-ml vial. A Teflon serum cap liner is placed on the vial and secured with a screw cap. By use of a 1-ml gastight syringe, 0.750 ml of cold (0°C) carbon disulfide and 1-bromohexane mixture is injected through the septum into the vial containing charcoal. The vial is then placed in an ultrasonic cleaner containing ice and water for 30 min. The sample containing charcoal in contact with carbon disulfide is subsequently stored at ≤ 0°C until GC separation and analyses are performed.

Analyses

Column preconditioning--

Before initial use, the chromatographic column is heat-treated to remove impurities. A flow of 20 to 30 ml/min of pure helium is established through the column, and the temperature is raised at 2°C/min from ambient to 200°C. This temperature is maintained for 40 h.

GC-MS conditions--

Typical operating conditions for the analyses of EDC with specific ion monitoring on a Hewlett-Packard 5992-A analyzer are as follows:

- helium — 0.45 atm
- injector temperature — 170°C

- oven temperature — 120°C isothermal
- solvent elution time — 5.3 min
- run time — 12.5 min
- electron multiplier voltage — indicated by autotune
- ion masses for EDC — 62, 49, 98, 100, and 102 m/e
- ion masses for 1-bromohexane — 57, 85 m/e
- dwell times — 750.0 ms for 62, 49, 57, 85 m/e; 500.0 ms for 98, 100, and 102 m/e
- selective ion monitoring window sizes — 0.10 m/e
- amount of carbon disulfide injected — 4 µl
- retention time of EDC — 6.4 min
- retention time of 1-bromohexane — 9.0 min

Sample injection--

The first step in the analysis is injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, the solvent flush injection technique should be used. A 10-µl syringe is flushed with solvent several times to moisten the barrel and plunger, then 1 µl of pure CS_2 is drawn into the syringe. The needle is removed from the solvent, and the plunger is pulled back approximately 0.5 µl to separate the solvent flush from the sample; a pocket of air is used as the marker. The needle is then immersed in the sample, and a 4-µl aliquot is withdrawn. The volume of the needle must be carefully selected, because the sample will be completely injected. After the needle is removed from the sample and before it is injected into the gas chromatograph, the plunger is pulled back 1 µl to minimize sample evaporation from the tip of the needle. The analyst should observe that the sample occupies 3.9 to 4.0 µl in the barrel of the syringe. When duplicate injections of a solution are made, no more than a 3 percent difference in area can be expected when the same syringe is used.

Measurement of area--

The areas of the EDC and 1-bromohexane peaks are determined by an electronic integration system capable of determining the area of all ions monitored at the same retention time. A printout of the area expressed in integration units is obtained. The most predominant ion or base peak in the mass spectrum of EDC, 62 m/e, is selected for quantitation. For 1-bromohexane, 85 m/e is selected for quantitation; this ion is not the base peak, but it is less subject to interference from other compounds than the base peak.

STANDARDS CALIBRATION AND ANALYSES

Preparation of Desorbing Solution and Standards

Preparation of desorbing solution (weekly)--

The analyst adds 5.0 µl of 1-bromohexane to a 250-ml volumetric flask containing 240 ml CS_2 and brings the flask to volume with CS_2. Concentration of the 1-bromohexane solution is 23.5 ng/µl.

Preparation of stock standard solution (weekly)--

The analyst adds 5.0 µl of pure EDC to a 10-ml volumetric flask containing 9.8 ml of the desorbing solution and brings the flask to volume with the desorbing solution. This yields an EDC concentration of 0.628 µg/µl.

Preparation of working standard procedure (daily)--

The analyst places 20 µl of the stock standard solution in a 5.0-ml volumetric flask containing 4.8 ml of the desorbing solution and brings the flask to volume with CS_2/1-bromohexane desorbing solution. This produces an EDC concentration of 2.512 ng/µl.

Calibration of the GC-MS System

The GC-MS system is set up according to the conditions previously described. Before use, the instrument is autotuned in accordance with the manufacturer's operations manual. Four µl of the working standard are injected onto the GC column and analyzed. A response ratio, based on the area obtained from the EDC

peak (ion 62) and divided by the area obtained from the 1-bromohexane peak (ion 85), is calculated and used to find the concentration of EDC in real samples. The response ratio is obtained by use of the following equation:

$$\text{response ratio} = \frac{A_1}{A_2} = R \qquad \text{(Eq. A-1)}$$

where A_1 = area of the EDC ion in integration units

A_2 = area of the 1-bromohexane ion in integration units

Since R is a ratio instead of an absolute area, variations between injections in the amount of sample or the detector response will not affect its value. The average response ratio is determined; no single response ratio must deviate from the average by more than ±5 percent. If a response ratio exceeds this limit, an error has occurred either during sample injection, in preparation of the working standard, or from instrument malfunction.

Analyses of Samples

Four µl are withdrawn from the desorbed sample solution consisting of the charcoal tube contents plus 750 µl of CS_2/1-bromohexane eluting reagent. The areas of 62 m/e ions from EDC and 85 m/e ions from 1-bromohexane are recorded. An injection of 4 µl of a standard in the range of the samples analyzed is inserted into every tenth sample. The response ratio is calculated and compared with the original calibration. An identically prepared blank tube is analyzed in the same manner. Any area resulting from the specific ion of 62 m/e is recorded.

CALCULATIONS

Uncorrected Sample Volume

The volume of air sample is left uncorrected for standard temperature and pressure because of the uncertainty associated with changes in average temperature and atmospheric pressure during 24-h sampling. The air sample volume taken for analysis is determined as follows:

$$V_m = \frac{F_1 + F_2}{2} \times T \times 10^{-6} \qquad \text{(Eq. A-2)}$$

where V_m = volume of gas sampled (uncorrected), m^3

F_1 = measured flow rate before sampling, ml/min

F_2 = measured flow rate after sampling, ml/min

T = sampling time, min

Ethylene Dichloride Concentration

Calculation of the EDC collected on the adsorption tube--

From the integrated areas for ion masses 62 and 85, the EDC content collected on the charcoal tube and corrected for the blank is calculated as follows:

$$W_{EDC} = \frac{(R_{spl} - R_{blk})}{R_{std}} \times C \times V \qquad \text{(Eq. A-3)}$$

where W_{EDC} = weight EDC, ng

$R_{spl} = \frac{\text{area EDC}}{\text{area 1-bromohexane}}$ (from sample)

$R_{blk} = \frac{\text{area EDC}}{\text{area 1-bromohexane}}$ (from blank)

$R_{std} = \frac{\text{area EDC}}{\text{area 1-bromohexane}}$ (from standard)

C = concentration of standard, ng/µl

V = volume of CS_2 and 1-bromohexane desorbing solution mixture used to desorb the charcoal tube (750 µl under normal conditions)

Calculation of EDC concentration*--

The concentration of EDC as $\mu g/m^3$ in the sampled ambient air is calculated as follows:

*The overall method efficiency was determined as 90 ±10 percent. A correction factor of 1.1 may be used if desired. C_{EDC} is multiplied by 1.1 to obtain the concentration corrected for method efficiency. For levels in excess of 10 µg/m^3, the backup adsorption tube is analyzed and the concentration added to the results from the first adsorption tube. In this case, no correction factor is recommended.

$$C_{EDC} = \frac{W_{EDC}}{Vm} \times 10^{-3} \qquad \text{(Eq. A-4)}$$

where C_{EDC} = concentration of EDC in the ambient air sampled, $\mu g/m^3$

W_{EDC} = weight of EDC, corrected for the blank, ng

Vm = volume of air sampled under sampling conditions, in m^3

The concentration of EDC may be calculated as parts per billion EDC:

$$ppb = \mu g/m^3 \times 0.247. \qquad \text{(Eq. A-5)}$$

EFFECTS OF STORAGE

Although little is known about the effects of storing charcoal tubes containing adsorbed EDC, some evidence indicates that compounds with chemical characteristics similar to EDC are adversely affected by strong sunlight and heat. Tubes should be stored in a dark place and at a low temperature. Carbon disulfide/1-bromohexane solutions of EDC in the $\mu g/m^3$ range are stable for at least 1 month if they are refrigerated in a sealed serum bottle with minimum head space. Information is unavailable on the effects of storage of samples containing other active substances commonly found in ambient air.

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